



(11) (A) No. 1 142 714

(45) ISSUED 830315

(52) CLASS 9-61

(51) INT. CL. D21C 3/00

(19) (CA) **CANADIAN PATENT** (12)

(54) PROCESS FOR THE PREPARATION OF AN AGENT  
WHICH CONTAINS ORGANIC, CYCLIC COMPOUNDS WITH  
KETO AND/OR HYDRO GROUPS AND SURFACEACTIVE  
AGENTS, AND PROCESSES FOR THE PRODUCTION  
OF PULP USING THIS AGENT

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(21) APPLICATION No. 354,578

(22) FILED 800623

(30) PRIORITY DATE Germany (Federal Republic of)  
(P 29 25 545.6) 790625

No. OF CLAIMS 11 - NO DRAWING

Canada

Process for the preparation of an agent which contains organic, cyclic compounds with keto and/or hydro groups and surface-active agents, and processes for the production of pulp using this agent

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Abstract of the Disclosure

Process for the preparation of organic cyclic compounds with keto and/or hydroxyl groups in granulated form. The granules such obtained are especially suitable for use in the pulp production from ligno-cellulose materials.

It has been reported (see, for example, Bach, G. Fiehn, Zellstoff und Papier 21, 3 (1972); H.H.Holton, Pulp and Paper Canada 78, 19 (1977); U.S. Patent Specification 4,012,280; U.S. Patent Specification 4,036,680; U.S. Patent Specification 4,036,681; Canadian Patent Specification 986,662; Japanese Laid-Open Specification 112,903/75; Japanese Laid-Open Specification 43,403/76; Japanese Laid-Open Specification 109,303/76 and East German Patent Specification 98,549) that anthraquinone derivatives and certain diketohydroanthracenes have a favourable action in certain processes for the production and bleaching of pulp from lignocellulose materials, such as wood, straw and bagasses, when they are employed in amounts of 0.001 to 10% by weight, relative to the lignocellulose material. Besides anthraquinone, anthrahydroquinone and Diels-Alder adducts of butadiene and its derivatives and p-benzoquinone or 1,4-naphthoquinone, the mono- and poly-alkyl, -alkoxy, -amino, -hydroxy and/or -sulpho derivatives of these compounds are also recommended for this. In the following text, these substances are collectively termed additives.

The additives are in general accessible in the form of powders. However, introduction of such pulverulent additives into processes for the production of pulps from lignocellulose materials and for bleaching of the pulps presents problems. When the pulverulent additives are added to the lignocellulose material to be employed, it should be taken into consideration that the finer constituents of the additives pass into the environment in the form of a dust and are thus partly withdrawn from the intended use, are a nuisance to persons working in the vicinity of the point of addition and can give rise to the danger of dust explosions. Furthermore, uniform distribution of the relatively small amounts of the required additive is

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difficult. However, uniform distribution of the additive is desirable in order to achieve a uniform pulp quality.

Uniform distribution of the additives is moreover made more difficult by the fact that the additives are in general only very slightly soluble in water and in the aqueous electrolyte solutions used for the production of pulp (for example only  $6 \cdot 10^{-4}$  g of 9,10-anthraquinone dissolve in 1 l of water at  $50^{\circ}$ ).

Furthermore, the additives are so poorly wetted by water and aqueous electrolyte solutions such as are used in the  
10 production of pulp that the finer constituents of the pulverulent additives cannot be stirred in or can be stirred in only with difficulty and float on the surface in the unwetted state, air being included in some cases. The additives moreover have a relatively high specific density (for example anthraquinone has a specific density of  $1.438 \text{ g/cm}^3$  at  $20^{\circ}\text{C}$ ), so that the coarser constituents of the pulverulent additives which can be stirred into water or the electrolyte solution rapidly settle again, and after the  
20 mixture has stood for a short time, a compact layer which can only be stirred up again with difficulty is formed on the bottom of the vessel. Introduction of the additives directly into the digesting liquor, into the mixture of lignocellulose material and digesting liquor or in the form of a slurry in water or dilute electrolyte solutions is thus likewise no reliable way of achieving uniform distribution of the additives.

The present invention now provides granules of an organic cyclic compound containing keto and/or hydroxyl groups, suitable for use in the production and bleaching of pulp from

lignocellulose materials, said compound being selected from the group consisting of (a) p-benzoquinone, (b) 1,4-naphthoquinone, (c) 9,10-anthraquinone, (d) Diels-Alder adducts of a 1,3-diene and p-benzoquinone or 1,4-naphthoquinone, (e) monoalkyl, dialkyl, hydroxyl, amino, alkoxy or alkylamino derivatives of such compounds, and (f) the reduced forms of (a) to (e), said granules comprising 60 to 99 % by weight of said organic cyclic compound, and 40 to 1 % by weight of surface active agent.

Organic cyclic compounds containing keto and/or hydroxyl groups which can be employed in the granules according to the invention are, for example, 9,10-anthraquinone, 2-methyl-anthraquinone, 2-ethylanthraquinone, 2,3-dimethyl-9,10-anthraquinone, 2,6-dimethylanthraquinone, 2,7-dimethylanthraquinone, 2-aminoanthraquinone, 1-methoxyanthraquinone, 1,4,4a,9a-tetrahydro-9,10-diketoanthracene, 2-ethyl-1,4,4a,9a-tetrahydro-9,10-diketoanthracene, 2,3-dimethyl-1,4,4a,9a-tetrahydro-9,10-diketoanthracene, 1,4,4a,5,8,8a,9a,10a-octahydro-9,10-diketoanthracene, 1,3-dimethyl-1,4,4a,9a-tetrahydro-9,10-diketoanthracene and 2,3,6,7-tetramethyl-1,4,4a,5,8,8a,9a,10a-octahydro-9,10-diketoanthracene. 2 or more of these substances can also be employed. It is also possible to use compounds which carry 2 or more of the substituents mentioned, for example hydroxyl groups and amino groups. Preferably, however, only one of the substances is employed, and 9,10-anthraquinone is very particularly preferred.

The organic, cyclic substances containing keto and/or hydroxyl groups, in particular 9,10-anthraquinone, are employed in preparing the granules according to the invention in a finely

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divided form. For example, the organic, cyclic compounds containing keto and/or hydroxyl groups, in particular 9,10-anthraquinone, can consist to the extent of at least 80% by weight of

particles with particle sizes of less than 10  $\mu\text{m}$ .  
The organic, cyclic substances containing keto and/or  
hydroxyl groups, in particular 9,10-anthraquinone,  
preferably consist to the extent of at least 80% by  
5 weight of particles with a particle size of less than  
5  $\mu\text{m}$ .

The organic, cyclic compounds containing keto  
and/or hydroxyl groups can be converted into such a  
finely divided form by grinding. Such a grinding  
10 operation can be carried out, for example, using the  
customary apparatuses for dry comminution, such as ball  
mills, rotor-stator mills, pinned disc mills, hammer  
mills and jet mills, if appropriate with suitable down-  
stream sifters. The jet mills can be operated, for  
15 example, with air or steam.

Virtually all the cationic, non-ionic and  
anionic surface-active agents can be employed as the  
surface-active agents in the process according to the  
invention.

20 Examples of possible cationic surface-active  
agents are quaternary long-chain and/or oxyethylated  
amines, quaternary pyridinium compounds or long-chain  
phosphonium compounds. Long-chain in this context  
means a carbon chain with at least 4 C atoms, preferably  
25 with at least 6 C atoms.

Particular examples of cationic surface-active  
agents are: trimethyl-hexadecyl-ammonium bromide, cetyl-  
pyridinium bromide, lauryl-dimethylbenzyl-ammonium  
chloride, monoesters of triethanolamine with stearic  
30 acid in the form of formic acid salts or acetic acid  
salts, N-lauryl-methylbenzimidazole hydrochloride and  
dodecyl-trimethyl-phosphonium bromide.

Most of these compounds and other cationic  
surface-active agents which can be used are described,  
35 for example, in K. Lindner, Tenside - Textilhilfsmittel -  
Waschrohstoffe (Surface-active Agents - Textile  
Auxiliaries - Detergent Bases), Volume 1, pages 963 to  
1041 (1964).

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Examples of possible non-ionic surface-active agents are addition products of alkylene oxides, in particular ethylene oxide, and higher fatty acids, alcohols, phenols, acid amides, mercaptans, amines or alkylphenols. The addition products can be obtained, for example, from 5 to 50 mols of alkylene oxide and 1 mol of fatty acid, alcohol, phenol, acid amide, mercaptan, amine or alkylphenol containing at least 4, preferably at least 6, C atoms. Other possible non-ionic surface-active agents are addition products of alkylene oxides, in particular ethylene oxide, and polypropylene oxide or sugars, as well as oxyethylated and non-oxyethylated sugar derivatives, such as fatty acid esters of pentaerythritol or of sucrose.

Particular examples of non-ionic surface-active agents are addition products of 5 to 20 mols of ethylene oxide and stearic acid, oleyl alcohol, polypropylene glycol, nonylphenol, oleic acid amide or dodecylamine.

Most of these compounds and other non-ionic surface-active agents which can be used are described, for example, in N. Schönfeldt, Grenzflächenaktive Ethylenoxid-Addukte (Surface-Active Ethylene Oxide Adducts), pages 42 to 95 (1976) and in K. Lindner, Tenside - Textilhilfsmittel - Waschrohstoffe (Surface-Active Agents - Textile Auxiliaries - Detergent bases), Volume 1, pages 837 to 917 (1964).

Anionic surface-active agents are preferably employed in the granules according to the invention. Examples of possible anionic surface-active agents are alkylsulphonates, sulphated unsaturated higher fatty acids, sulphonates of polycarboxylic acid esters, alkylbenzenesulphonates, sulphated aliphatic alcohols,



adducts of ethylene oxide and higher amines, acids, phenols or alcohols, which adducts have been converted to acid esters with an inorganic polybasic acid, such as phosphoric acid or especially sulphuric acid, as well as ligninsulphonates or derivatives of ligninsulphonates, condensation products of aromatic sulphonic acids and formaldehyde, and polyphosphates.

Particular examples of anionic surface-active agents are:  
 sodium dodecylsulphonate, sodium laurylsulphate, sodium dodecylbenzenesulphonate, diisobutyl-naphthalenesulphonate, acid  
 10 sulphuric acid esters of the addition product of 2 mols of ethylene oxide and 1 mol of nonylphenol, sodium dioctylsulphosuccinate, condensation products of cresol, 2-naphthol-6-sulphonic acid and formaldehyde, and sulphonic acids of naphthalene, terphenyl or ditolyl ether, in each case as condensation products with formaldehyde. All the anionic surface-active agents are preferably employed in the form of their alkali metal salts and/or ammonium salts.

Most of these compounds are other anionic surface-active agents which can be used are described in K. Lindner, Tenside -  
 20 Textilhilfsmittel - Waschrohstoffe (Surface-Active Agents - Textile Auxiliaries - Detergent Bases), Volume 1, pages 571 to 835 (1964).

Lignin-sulphonates and/or condensation products of aromatic sulphonic acids and formaldehyde, for example the lithium, sodium, potassium, magnesium, calcium and/or ammonium salts of lignin-sulphonic acid, are particularly preferably employed as surface-active agents in the granules according to the

invention. Any desired mixtures of anionic and non-ionic surface-active agents can also be employed.

The surface-active agents can be employed, for example, in an amount such that the dried granules contain 60 to 99% by weight of organic, cyclic compounds with keto and/or hydroxyl groups and 40 to 1% by weight of surface-active agents. The surface-active agents are preferably employed in an amount such that the dried granules contain 80 to 90% by weight of organic, cyclic compounds with keto and/or hydroxyl groups and 20 to 10% by weight of surface-active agents.

The preparation of the granules according to the invention can be carried out by a procedure in which the organic, cyclic compounds containing keto and/or hydroxyl groups are mixed with the surface-active agents, this mixture is ground, the ground mixture is then sprayed with water or an aqueous liquid and the granules thus formed are dried. It is also possible to grind the surface-active agents separately in a manner corresponding to that for the organic, cyclic compounds containing keto and/or hydroxyl groups, and to mix them, in the ground form, with the ground organic, cyclic compounds containing keto and/or hydroxyl groups. It is furthermore also possible to dissolve the surface-active agents in water and to use an aqueous solution of this type to spray the ground organic, cyclic compounds containing keto and/or hydroxyl groups. Moreover, some of the surface-active agents can be ground together with or separately from the organic, cyclic compounds containing keto and/or hydroxyl groups, the ground surface-active agents and the ground organic, cyclic compounds containing keto and/or hydroxyl groups can be mixed

and the remainder of the surface-active agents can be added to the water or the aqueous liquid used for spraying. The preparation of the granules according to the invention is preferably carried out by a procedure in which the surface-active agents are ground together with the organic, cyclic compounds containing keto and/or hydroxyl groups.

If agents prepared according to the invention are to be used in pulp production processes which are carried out in an alkaline medium, it can be advantageous to add small amounts of an alkaline substance to the organic, cyclic compounds containing keto and/or hydroxyl groups before the grinding or to the water or the aqueous liquid before the spraying. Such alkaline substances, in particular alkaline salts, can furthermore first be ground in a manner corresponding to that for the organic, cyclic compounds containing keto and/or hydroxyl groups and then mixed, in the ground form, with the ground organic, cyclic compounds containing keto and/or hydroxyl groups, before the spraying.

Examples of suitable

alkaline substances to be added are NaOH, KOH, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub> and/or LiOH. Alkaline substances can be added in amounts of, for example, 0.2 to 5% by weight (relative to the finished granules). Such substances are  
5 preferably added to the water or to the aqueous liquid used for spraying.

If the agents prepared according to the invention are to be converted into an aqueous dispersion before being used in a process for the production of  
10 pulp, it can be advantageous, before grinding, to add to the organic, cyclic compounds containing keto and/or hydroxyl groups substances which have a stabilising effect on dispersions. Such substances can also first be ground in a manner corresponding to that for the  
15 organic, cyclic compounds containing keto and/or hydroxyl groups and can then be mixed, in the ground form, with the ground organic, cyclic compounds containing keto and/or hydroxyl groups. Substances which have a stabilising effect on dispersions can be, for example:  
20 highly disperse silicic acid, magnesium silicates and aluminium silicates, montmorillonites, which can also contain organic base, chalk and/or thickeners, such as methylcellulose, hydroxymethylcellulose, hydroxyethylcellulose or carboxymethylcellulose, as well as poly-  
25 acrylates and/or polymethacrylates and/or copolymers thereof, and combinations of the substances mentioned. Such substances can be added in amounts of, for example, 0 to 5% by weight, preferably 0.1 to 1% by weight (in each case relative to the finished granules).

30 Furthermore, preservatives can be added to the organic, cyclic compounds containing keto and/or hydroxyl groups and/or to the water or to the aqueous liquid used for spraying. Possible preservatives are, for example, substances which prevent the formation of  
35 mould and/or bacterial attack. Substances which are suitable are the customary preservatives, for example sodium pentachlorophenate and addition products of

paraformaldehyde and aromatic alcohols, in particular benzyl alcohol. Preservatives can be added in amounts of, for example, 0 to 3% by weight, preferably in amounts of 0.05 to 0.5% by weight (in each case relative to the finished granules). If the preservatives are insoluble or poorly soluble in water, they are preferably added to the organic, cyclic compounds containing keto and/or hydroxyl groups before grinding, or are ground separately in a manner corresponding to that for the organic, cyclic compounds containing keto and/or hydroxyl groups and mixed, in the ground form, with the ground organic, cyclic compounds containing keto and/or hydroxyl groups. Water-soluble preservatives are preferably added to the water or to the aqueous liquid used for spraying.

It can be advantageous to introduce other constituents, if appropriate in addition to alkaline substances and/or preservatives, in the preparation of the agent according to the invention. Such other constituents can be, for example, inorganic salts, carbohydrates, urea, urea derivatives and/or water-soluble polymers.

The abovementioned inorganic salts, urea and urea derivatives, carbohydrates and/or water-soluble polymers can in general be added to the water or to the aqueous liquid used for spraying and/or to the organic, cyclic compounds containing keto and/or hydroxyl groups before or after these are ground. If they are added after the grinding of the organic, cyclic compounds containing keto and/or hydroxyl groups, they are appropriately ground separately in the same manner as the organic, cyclic compounds containing keto and/or hydroxyl groups.

Examples of inorganic salts are chlorides and sulphates of alkali metals, magnesium or ammonium, in particular magnesium sulphate, potassium sulphate, sodium sulphate, potassium chloride, ammonium sulphate,

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lithium sulphate and ammonium chloride. Such compounds can be added, for example, in amounts of 0 to 80% by weight, preferably 0 to 20% by weight (relative to the finished granules). Inorganic salts are preferably added to the organic, cyclic compounds containing keto and/or hydroxyl groups before these are ground.

Urea and urea derivatives can be added, for example, in amounts of 0 to 20% by weight, preferably 0 to 10% by weight (relative to the finished granules). Urea or urea derivatives are preferably added to the organic, cyclic compounds containing keto and/or hydroxyl groups before these are ground.

Examples of carbohydrates are starch, sugars, methylcellulose and hydroxypropylmethylcellulose. These compounds can be added, for example, in amounts of 0 to 20% by weight, preferably 0 to 10% by weight (relative to the finished granules). Carbohydrates can be added to the organic, cyclic compounds containing keto and/or hydroxyl groups before these are ground and/or to the water used for spraying.

Examples of water-soluble polymers are polyvinyl alcohol, polyvinylpyrrolidone and mixtures of cane sugar and sodium salts of polymeric carboxylic acids and polyoxyethylene ethers. These compounds can be added, for example, in amounts of 0 to 15% by weight, preferably 0 to 8% by weight (relative to the finished granules). Water-soluble polymers are preferably added to the water used for spraying.

All these additives have the advantage that they promote the formation of bridges between the individual particles of the organic, cyclic compounds containing keto and/or hydroxyl groups, and the build-up of the granules is thus facilitated.

If alkaline substances, preservatives, inorganic salts, urea or urea derivatives, carbohydrates and/or water-soluble polymers are also used, in addition to the surface-active agents, in preparing the agents according

to the invention, the total sum of these additions (including the surface-active agents) is advantageously not more than 30% by weight (relative to the finished granules).

- 5           The water or the aqueous liquid used for spraying can also contain organic water-miscible solvents. Such solvents can be, for example, alcohols, in particular those with 1 to 8 C atoms, for example methanol, ethanol, isopropanol and butanol. Such solvents can
- 10 be added to the water or to the aqueous liquid in amounts of, for example, 0 to 40% by weight (relative to the water), and have the advantage that they can effect better surface-wetting of the organic, cyclic compounds containing keto and/or hydroxyl groups.
- 15           It is furthermore possible to use liquids which contain water, if appropriate surface-active agents, and one or more of the abovementioned additives, in any desired combination, for the spraying.
- 20           The finely divided organic, cyclic compounds with keto and/or hydroxyl groups which can optionally contain the additives described can be sprayed with water or an aqueous liquid in customary apparatuses for forming granules by layering. For example, mixing granulators, screen granulators, disc granulators,
- 25 extruders and fluidised bed or moving bed granulators can be used for this purpose. The granulation can be carried out either discontinuously or continuously. The spraying is carried out with water or an aqueous liquid, which can contain the constituents described
- 30 above, in an amount of 5 to 30% by weight of water or aqueous liquid (relative to the finely divided constituents). This amount is preferably 5 to 15% by weight. Customary nozzles can be used for the spraying. Two-material nozzles are preferably used, in order to produce
- 35 as fine as possible a spray mist.

The spraying can be carried out, for example, at 10 to 60°C and under pressures in the range from 0.5 to

2.5 bar. Spraying is preferably carried out at room temperature up to 40°C, and under pressures in the range from 1 to 2 bar.

After the spraying, moist granules are present.

- 5 According to the invention, these are subsequently dried. The customary drying apparatus can be used for the drying, for example tubular dryers, circulating air drying cabinets, drying belts or freeze-dryers. Fluidised bed or moving bed dryers are preferably employed.
- 10 Suitable drying conditions are, for example, temperatures in the range from 40 to 90°C and pressures in the range from 0.5 to 2.5 bar. Drying is preferably carried out at temperatures in the range from 60 to 80°C and under pressures in the range from 1 to 2 bar.
- 15 It can be advantageous to remove dust-like and coarser agglomerates from the resulting dry granules by sieving. The customary sieving machines can be used for this purpose. The granules prepared according to the invention preferably have, if appropriate after
- 20 sieving, a particle diameter in the range from 0.1 to 5 mm, preferably in the range from 0.2 to 2 mm. The finer constituents can optionally be recycled again to the spraying, and the coarser constituents can optionally be recycled to the grinding.
- 25 The agents prepared according to the invention can have a very high content of the actual active substance from the group of organic, cyclic compounds containing keto and/or hydroxyl groups, and this content can be, for example, 80 to 90% by weight (relative to
- 30 the finished granules). When introduced into water or into digestion solutions customary in the production of pulp (for example by the kraft process or soda process), the agents prepared according to the invention spontaneously form dispersions in which the organic,
- 35 cyclic compounds containing keto and/or hydroxyl groups are present predominantly with particle sizes of less than 10 µm. Optimum use of the favourable effects of



the presence of these compounds in processes for the production of pulp can thus be made, since uniform distribution of these compounds is achieved in a simple manner.

5 The agents prepared according to the invention do not change under customary storage conditions, even on prolonged storage. Because of their granular nature, they are readily free-flowing, can easily be metered and can be handled with a high degree of safety.

10 Customary layered granules which are used in industry, for example in the field of dyestuffs, plant protection agents and pharmaceuticals, and which have been produced in a manner similar to the granules produced according to the invention in general contain 5  
15 to at most 70% by weight of the substance essential for the use. Surprisingly, granules which contain up to 90% by weight and more of organic, cyclic compounds with keto and/or hydroxyl groups can be prepared by the process according to the invention. Such highly concentrated  
20 granules have the advantage that, on the one hand, small amounts of additives are used, and the transport costs and the risks during use are thus kept at a low level, but on the other hand, however, a substance form which disperses readily is obtained.

25 The present invention relates to a process for the production of pulp from lignocellulose materials in the presence of organic, cyclic compounds containing keto and/or hydroxyl groups, which is characterised in that the organic, cyclic compounds containing keto and/  
30 or hydroxyl groups are employed in the form of the agent prepared according to the invention.

By the term "process for the production of pulp", there are to be understood all processes and process stages in which lignin in materials containing lignin  
35 and cellulose is subjected to chemical treatment. Examples in this context are alkaline, neutral and acid digestion processes on lignocellulose materials, such as

wood, straw, bagasses and grass, and bleaching processes on lignocellulose materials which have been partially or largely digested.

Apart from the use of the agents prepared according to the invention, the production of pulp by the process according to the invention can be carried out in a manner which is in itself known. For example, this process can be carried out by digesting lignocellulose materials in a sulphite solution, which can be acid, neutral or alkaline, and the agent prepared according to the invention can be added to the digestion solution before or after addition of the lignocellulose material. The agent prepared according to the invention can also be employed in the known pulp production processes, which are known as the kraft process, soda process and polysulphide process. The agent prepared according to the invention can furthermore be employed in the known oxygen/alkali process for the production of pulp and/or in the bleaching processes known for the production of pulp.

The agent prepared according to the invention can be employed in the process, according to the invention, for the production of pulp and for bleaching pulp in an amount of, for example, 0.001 to 10% by weight (relative to the lignocellulose material). 9,10-Anthraquinone in the form of the agent prepared according to the invention is preferably employed in the process, according to the invention, for the production of pulp. The use of the agent mentioned as preferred in the context of the agents prepared according to the invention is particularly preferred.

The process, according to the invention, for the production of pulp has a number of advantages. Thus, for example, metering and uniform distribution of organic, cyclic compounds containing keto and/or hydroxyl groups can be effected without difficulties, and as a result pulps of uniform quality are obtained. It is

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furthermore possible to realise the positive effects, established under ideal conditions on a laboratory scale, of the addition of organic, cyclic compounds containing keto and/or hydroxyl groups to large-scale industrial  
5 plant for the production of pulp.

In the laboratory experiments, for example, the lignocellulose material was agitated in the digestion liquid or bleaching liquid, and this facilitated distribution of the additives. In large-scale industrial  
10 trial plants for the production of cellulose, such agitation is carried out only to a minor extent and distribution of the additives is thus made more difficult if they are not used in the form of the agents prepared according to the invention.

#### 15 Examples

In the following text, the abbreviation PW means parts by weight.

##### Example 1

80 PW of 9,10-anthraquinone were mixed with 18  
20 PW of spray-dried sulphite waste liquor, containing lignin-sulphonates, and 2 PW of sodium diisobutyl-naphthalene sulphonate, and the mixture was jet-milled. Thereafter, the particle size of the pulverulent mixture was less than 10  $\mu$ m. This pulverulent mixture was  
25 granulated in a mixing granulator with grinding elements, whilst spraying with 8% by weight of water (relative to the pulverulent mixture). After drying the granules, the particles with a particle size in the range from 0.2 to 2.0 mm were sieved off. The pro-  
30 duct was free from dust and could be dispersed spontaneously in water. The product can be metered by volume and could easily be stirred into a digestion liquor for wood.

##### Example 2

35 The process followed was as in Example 1, but 85 PW of 9,10-anthraquinone, 13 PW of spray-dried sulphite waste liquor, containing lignin-sulphonates,

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and 2 PW of sodium diisobutylnaphthalene sulphonate were employed and the pulverulent mixture was granulated in a screen granulator. The product thus obtained had the same properties as the product from Example 1.

5 Example 3

The procedure followed was as in Example 1, but 75 PW of 9,10-anthraquinone, 23 PW of spray-dried sulphite waste liquor, containing lignin-sulphonates, and 2 PW of sodium diisobutylnaphthalene sulphonate were employed and the pulverulent mixture was granulated in a disc granulator. The product thus obtained had the same properties as the product from Example 1.

Example 4

The procedure followed was as in Example 1, but 15 90 PW of 9,10-anthraquinone, 2 PW of sodium diisobutylnaphthalene sulphonate and 8 PW of spray-dried sulphite waste liquor were granulated in a fluidised bed granulator (manufacturer: Aeromatik, Muttenez, Switzerland). The product thus obtained had the same properties as the 20 product from Example 1. The product could easily be stirred into the digestion liquors for wood which are used in the kraft process and soda process.

Example 5

80 PW of 1,4-benzoquinone were mixed with 18 PW 25 of spray-dried sulphite waste liquor, containing lignin-sulphonates, and 2 PW of sodium diisobutylnaphthalene sulphonate, and the mixture was jet-milled. Thereafter, the particle size of the pulverulent mixture was less than 10  $\mu\text{m}$ . This pulverulent mixture was 30 granulated in a fluidised bed granulator (manufacturer: Aeromatik, Muttenez, Switzerland), whilst spraying with 9% by weight of water (relative to the pulverulent mixture). After drying the granules, the particles with a particle size in the range from 0.2 to 2.0 mm were 35 sieved off. The product was free from dust and free-flowing and could be dispersed spontaneously in water.

Example 6

The procedure followed was as in Example 5, but 90 PW of 2-aminoanthraquinone, 8 PW of spray-dried sulphite waste liquor, containing lignin-sulphonates, and 2 PW of sodium diisobutyl naphthalene sulphonate were employed and the mixture was granulated whilst spraying with 8% by weight of water. The constituents with particle sizes of less than 0.2 mm and more than 2.0 mm sieved out after drying were recycled into the process. The product could readily be stirred into so-called white liquor (= aqueous solution of the digestion chemicals) in the kraft process and soda process and spontaneously formed a dispersion in this liquor.

Example 7

The procedure followed was as in Example 4, but a continuously operating moving bed granulator (moving bed unit 38, manufacturer: Anhydro, Copenhagen, Denmark) was used instead of the discontinuously operating fluidised bed granulator.

When stirred into water or a digestion liquor, for wood, of the kraft process or soda process, the product spontaneously gave very fine dispersions.

Example 8

The procedure followed was as in Example 6, but a moving bed granulator according to Example 7 was used.

When stirred into water or a digestion liquor, for wood, of the kraft process or soda process, the product spontaneously gave very fine dispersions.

Example 9

The procedure followed was as in Example 4, but the following substances were employed:

	Organic, cyclic compound containing keto and/or hydroxyl groups (PW)	Spray-dried sulphite waste liquor (PW)	Sodium diisobutyl naphthalene sulphonate (PW)
5	1-Methyl-anthraquinone (70)	28	2
	1,5-Dimethyl-anthraquinone (80)	17	3
	1-Hydroxyanthraquinone (75)	22	3
	1,5-Dihydroxyanthraquinone (80)	18	2
10	1-Methyl-8-amino- anthraquinone (75)	23	2

Granules which disperse spontaneously in kraft digestion liquors and soda digestion liquors, are free from dust and free-flowing and can be metered by volume  
15 were obtained.

Example 10

80 PW of 9,10-anthraquinone, 8 PW of spray-dried sulphite waste liquor, containing lignin-sulphonates, 2 PW of sodium diisobutyl naphthalene sulphonate and 10  
20 PW of urea were mixed, and the mixture was jet-milled. Thereafter, the particle size of the pulverulent mixture was less than 10  $\mu$ m. This mixture was granulated in the same manner as described in Example 1. The product was free from dust and could be dispersed spon-  
25 taneously in water. The product can be metered by volume and could readily be stirred into a digestion liquor for wood.

Example 11

The procedure followed was as in Example 10, but  
30 10 PW of polyvinyl alcohol were employed instead of urea. The properties of the product were as indicated in Example 10.

Example 12

The procedure followed was as in Example 10, but  
35 10 PW of sugar were employed instead of urea. The properties of the product were as indicated in Example 10.

Le A 19 408

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. Granules of an organic cyclic compound containing keto and/or hydroxyl groups, suitable for use in the production and bleaching of pulp from lignocellulose materials, said compound being selected from the group consisting of (a) p-benzoquinone, (b) 1,4-naphthoquinone, (c) 9,10-anthraquinone, (d) Diels-Alder adducts of a 1,3-diene and p-benzoquinone or 1,4-naphthoquinone, (e) monoalkyl, dialkyl, hydroxyl, amino, alkoxy or alkylamino derivatives of such compounds, and (f) the reduced forms of (a) to (e), said granules comprising 60 to 99 % by weight of said organic cyclic compound, and 40 to 1 % by weight of surface active agent.
2. Granules of 9,10-anthraquinone according to claim 1.
3. Granules according to claim 1 containing 80 to 90 % by weight of the organic cyclic compound and 10 to 20 % by weight of the surface active agent.
4. Granules according to claim 1, wherein the surface active agents are anionic surface active agents.
5. Granules according to claim 1, wherein at least 80 % by weight of the organic cyclic compound employed has a particle size of less than 10  $\mu$ .
6. Granules according to claim 5, wherein the surface active agent is a lignin sulphonate, a derivative of a lignin sulphonate and/or a condensation product of an aromatic sulphonic acid and formaldehyde.

7. Granules according to claim 1, additionally containing 0.2 to 5 % by weight of an alkaline substance.
8. Granules according to claim 1, containing additionally a substance which has a stabilising effect on dispersions, a preservative, an inorganic salt, urea, a urea derivative, a carbohydrate and/or a water soluble polymer.
9. Granules according to claim 1, having a particle size in the range from 0.1 to 5 mm.
10. In the process of digestion of lignocellulosic material to produce pulp, wherein to the digestion liquor there is added an organic cyclic compound as digestion aid, the improvement which comprises adding said organic cyclic compound in the form of granules according to claim 1.
11. In the process of alkaline digestion of lignocellulosic material to produce pulp, wherein to the digestion liquor there is added an organic cyclic compound as digestion aid, the improvement which comprises adding said organic cyclic compound in the form of granules according to claim 5.

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PATENT AGENTS





**SUBSTITUTE**

***REMPLACEMENT***

**SECTION is not Present**

***Cette Section est Absente***